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Recycling coffee silverskin in sustainable composites based on a poly (butylene adipate-co-terephthalate)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) matrix

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ABSTRACT

This work investigates the feasibility of using coffee silverskin (CSS), one of the most abundant coffee waste products, as a reinforcing agent in biopolymer based composites. The chemical composition, antioxidant activity and morphology of CSS were studied by specific chemical essays and scanning electron microscopy, whilst the thermal stability and the functional groups available on the surface were investigated by thermogravimetric analysis and infrared spectroscopy, respectively. The thermal stability and fibrous structure of CSS make it suitable as a reinforcing filler in polymer composites, which was confirmed by manufacturing biocomposites with improved stiffness and tensile strength, not degraded by CSS addition when compared to the neat biopolymer.

1. Introduction

Coffee currently represents one of the most frequently consumed drinks in the world and one of the most essential agricultural commodities, as confirmed by an exported value of almost $30.8 billion in 2016 (www.trademap.org/tradestat, 2016), and world exports equal to 10.44 million bags in June 2017, compared with 9.88 million in June 2016 (http://www.ico.org, 2017). Coffee beans can be obtained by over 70 species belonging to the plant *Coffea L.*, however only two species are of commercial importance, namely *Coffea arabica* (Arabica), considered as the noblest of all coffee plants and providing 75% of world's production, and *Coffea canephora* (Robusta), which accounts for about 24% of world's production (Mussatto et al., 2011; Narita and Inouye, 2014). Many processing steps are involved in the industrial production of coffee beverage starting from the green coffee cherries and the great worldwide demand of this product is the cause of serious environmental concerns mainly related to the huge amount of solid residues generated. In this regard, two are the main wastes that are in need of specific disposal options, namely coffee silverskin (CSS) and spent coffee grounds (SCG). Coffee silverskin is the by-product of the coffee roasting process and consists of the innermost layer of the coffee bean, while SCG is the residue of the brewing process (Esquivel and Jiménez, 2012). Neither CSS nor SCG have currently sound alternatives to landfill disposal. In particular CSS, being not economically valuable, is currently disposed of as a solid waste or simply burned while SCG, besides landfill disposal, has found some uses as a fertilizer. Both solid wastes have a remarkable and negative environmental impact because of their high organic content and the presence of compounds such as caffeine, tannins, and polyphenols. Also burning does not represent a suitable disposal option due to the potential release of greenhouse gases into the atmosphere.

This environmental awareness has therefore triggered, over the last years, the need to find much more effective disposal strategies which can also include their recycling into useful products, not only for coffee residues (Ashori and Nourbakhsh, 2010; Mitchell et al., 2014; Väisänen et al., 2016). In some cases, SCG has been used as fuel in industrial boilers of the same industry due to its high calorific power of over 20 MJ/kg, which is higher than that of other agro-industrial residues (Zuorro and Lavecchia, 2012). Kondamudi et al. (2008) confirmed the possible use of SCG as a source for the production of biodiesel and fuel pellets, in addition to other value-added products, such as H_2 and ethanol. The oil content of SCG (around 15%) can be successfully transformed into similar amounts of biodiesel by transesterification processes, while the remaining solid residue can be exploited in the production of ethanol (Sendzikiene et al., 2004) and fuel pellets (Kondamudi et al., 2008). Another possibility is represented by the

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supercritical fluid extraction of the lipid fraction from SCG, as investigated by Couto and co-workers (Couto et al., 2009). On the other hand, effective methods for the utilization of CSS have not been developed so far and most CSS is simply disposed of as industrial waste. Few exceptions include its use as combustible (Saenger et al., 2001) or the exploitation of its antioxidant capacity for new functional ingredients (Borrelli et al., 2004).

Unfortunately, none of these methods represents the best solution or the most efficient in terms of value addition, especially if one considers the large availability of such residues. In this framework, a quite recent alternative for the sustainable exploitation of these residues is their use as filler in new biodegradable materials (Mussatto et al., 2011). García-García et al. (2015) investigated the effect of a hydrophobic surface treatment of SCG powder with palmitoyl chloride and compared it with conventional treatments such as silanization with GLYMO and/or use of compatibilizers (PP-g-MA) in terms of mechanical, morphological and thermal properties as well as the effects on water absorption of polypropylene (PP)/SCG composites. The results showed that both treated and untreated SCG into a PP matrix promoted a slight decrease in flexural strength and a slight increase in flexural modulus. Use of conventional matrix modifiers, such as PP-g-MA in PP/SCG composites, did not lead to a significant increase in mechanical and thermal performance and the water uptake remained one of the main drawbacks. In a recent work, Lee et al. (2015) investigated the mechanical and optical properties of nanocomposites based on polyvinyl alcohol reinforced with SCG previously subjected to a ball milling process. The authors compared the performance of such nanocomposites with the one of carbon black-filled PVA highlighting the better deodorizing, mechanical, and optical behaviour of composites based on milled SCG. Wu (2015) investigated the morphology, mechanical properties, and biodegradability of composite materials based on polylactide (PLA) and SCG. In an attempt to improve interfacial adhesion, PLA was grafted with maleic anhydride and reinforced with surface-treated spent coffee grounds (TSCG) obtained by dissolving a mixture of crosslinking agents in a stoichiometric solution of tetraethyl orthosilicate (TEOS). The compatibilized formulation (PLA-g-MA/TSCG) showed increased interfacial adhesion that resulted in improved mechanical properties of the composites. The authors reported also a higher biodegradation in soil of PLA-g-MA/TSCG composites compared to that of neat PLA. Extracted spent coffee ground (ESCG) was used as filler to reinforce polypropylene by Wu et al. (2016) and the oil extraction was found to be beneficial to improve the interfacial adhesion between filler and PP matrix, even though the flexural and tensile strengths were lower compared to those of neat PP. Moustafa et al. (2017a) added SCG to poly(butylene adipate-co-terephthalate) (PBAT), pointing out the need to add a plasticizer (polyethylene glycol) to improve the tensile strength of the resulting composites compared to unplasticized ones (even though in both cases strength was lower than that of neat PBAT). In an attempt to increase hydrophobicity of SCG to promote a better interfacial adhesion with PBAT, Moustafa et al. (2017b) recently used a torrefaction pretreatment, which proved to be effective in enhancing the tensile strength of biocomposites compared to neat PBAT up to a 10 wt% of SCG.

On the contrary, to the best of authors' knowledge, few works can be found dealing with the use of CSS as filler in polymer matrices, with the exception of the studies authored by Barone (2009) and Zarrinbakhsh et al. (2016). In this framework, the aim of this study is to design new composite materials based on fully sustainable polymers modified via the inclusion of CSS to improve target properties (mechanical and thermal) with an additional objective related to the cost reduction of final products and the mitigation of environmental concerns related to the disposal of coffee waste material.

The use of PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) is still quite limited, which is due to the high price and inferior material properties compared to traditional commodity plastics, including low impact strength/toughness and susceptibility to molecular degradation via hydrolysis at high processing temperatures (Avella et al., 2007). Poly(butylene adipate-co-terephthalate) (PBAT) is an aliphatic–aromatic copolyester (made from fossil resources but biodegradable) that can be used as toughening agent in biodegradable and biobased polymers such as PLA and PHBV (Jiang et al., 2005). Biopolymer blends are definitely receiving increased attention as matrix material for composites, as they combine the major properties of both blending components. In this context, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), the prevailing class of polyhydroxyalkanoates, blended with an aliphatic-co-aromatic polyester, poly(butylene adipate-co-terephthalate) (PBAT), has good balance of stiffness and toughness properties, and it was already proved how these blends can be considered suitable for preparing composites based on natural fillers (Javadi et al., 2010; Nagarajan et al., 2013a, 2013b; Zhang et al., 2014).

To this effect, a pre-blend of PHBV/PBAT (65%PBAT-35%PHBV) is selected as a matrix material for this study.

2. Materials and methods

2.1. Materials

Coffee silverskin was obtained from a local coffee-roasting company in Rome (Italy) and was derived from a blend of 75% (w/w) Arabica and 25% (w/w) Robusta. CSS was used in the as-supplied state (Un) and also after a grinding and sieving process (S) leading to dimensions lower than 150 μm and stored in the dark at room temperature until use. A commercial grade of a biopolymer blend (65%PBAT-35%PHBV) by NaturePlast was used as matrix for biocomposites.

Methanol, ethanol, hydrochloric acid (37% w/w), sodium carbonate, sodium acetate, acetic acid, aluminum chloride and ferric chloride ($FeCl_3$•$6H_2O$) were purchased from Carlo Erba (Milano, Italy), while the Folin-Ciocalteu's phenol reagent, DPPH (2,2-diphenyl-1-picrylhydrazyl radical, ABTS (2,2-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid), potassium persulfate ($K_2S_2O_8$), Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), gallic acid, quercetin were obtained from Sigma-Aldrich (Milano, Italy). All chemicals were reagent grade and used without further purification.

2.2. Characterization of coffee silverskin

A three-stage extraction procedure was used to extract all phenolics and other antioxidant compounds from coffee silverskin. Each extraction was performed at 60 °C for 30 min, using aqueous ethanol (50% v/v) as solvent. The liquid-to-solid ratio was equal to 100, 50 and 25 mL g^{-1} in the first, second and third step, respectively. After separation from the solid by centrifugation (10,000*g* for 10 min), the extracts from the three stages were combined and assayed.

Total phenolics were determined by the Folin-Ciocalteu method as described elsewhere (Panusa et al., 2013). The results were expressed as gallic acid equivalents (GAE) per unit weight of dry solid using a calibration curve obtained with gallic acid standards.

Total flavonoids were determined in accordance with the method by Zhishen et al. (1999) with slight modifications. Specifically, 0.075 mL of 5% (w/v) sodium nitrite were added to 1.5 mL of diluted sample and the solution was left to react for 5 min. Then, 0.15 mL of aluminum chloride hexahydrate solution (10% w/v) were mixed. After 6 min, 0.5 mL of 1 M sodium hydroxide and 0.775 mL of distilled water were added and the absorbance at 510 nm was immediately measured. The amount of flavonoids was expressed as quercetin equivalents (QE) per unit weight of dry solid using a calibration curve obtained with quercetin standard solutions.

Antioxidant activity was determined by the DPPH, ABTS and FRAP assays according to the procedures described by Panusa et al. (2013) and Conde et al. (2009). Antioxidant capacity values were expressed as Trolox equivalents (TE) per unit weight of dry solid using calibration curves obtained with Trolox standards.